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Behavior of the interphase of dyed cotton residue flocks reinforced polypropylene composites.

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Abstract

Textile industry produces a high amount of residues that, nowadays, are poorly managed. The majority of such wastes are dumped and landfilled. Among all the textile value chain, cotton yarning factories produce wastes in the shape of fiber flocks, with lengths smaller than 10 mm that prevent their reintroduction in the textiles manufacturing process. Nonetheless, such waste cotton flocks could be used as reinforcement for short fiber mould injected composites. This paper reports on the behavior of the interphase between the cotton flocks and a polypropylene matrix. It was found that the organic dyes present on the cotton flocks seem to affect the quality of the interphase in two ways: on the one hand by increasing the affinity between the cotton fibers and the matrix, and on the other hand by limiting the effect of the coupling agents. Micromechanic models are used to further research the quality of the interphase and the intrinsic properties of the composites.

Keywords: A, Fabrics/textiles, fibres; B, Interphase, Strength; E, Injection molding

1 Introduction

Since the textile industry is generating huge amounts of residues, the increasing environmental consciousness and demands of legislative authorities is driving this sector to look for solutions to deliver the remainders into recycling processes and convert these waste products into valuable byproducts [1, 2]. However, the rate of textile recycling is still relatively low. On average, approximately 10 million tons of textile waste is currently dumped in Europe and America each year. Considering the

diversity of fibrous waste and structures, many technologies must work in concert in an integrated industry in order to increase the rate of recycling [3, 4].

Textiles represent about 3 wt.% of a household bin. At least 50% of the textiles we throw away are recyclable; however, the proportion of textile wastes reused or recycled annually is only around 25%. Although the majority of textile waste provides from household sources, waste textiles also arise during yarn and fabric manufacture, garment-making processes and from the retail industry. In this sense, textile waste can be classified as either pre-consumer or post-consumer. Pre-consumer textile waste consists of by-product materials from the textile, fiber and cotton industries. Each year 750,000 tons of this waste is recycled into new raw materials for the automotive, furniture, mattress, coarse yarn, home furnishings, paper and other industries. Through the efforts of this industry approximately 75% of the pre-consumer textile waste that is generated is diverted from our landfills and recycled. Some post-industrial waste is recycled 'in-house', usually in the yarn and fabric manufacturing sector. The rest, aside from going to landfill or incineration, is sent to merchants [5]. As an example, in Hong Kong, there are 253 tons of textiles through up to landfill daily, and the U.S. Environmental Protection Agency estimates that textile waste supposes nearly 5% of all landfill space. The post-consumer waste goes to jumble sales and charities but more typically are disposed of into the trash and end up in municipal landfills. Together, they provide a vast potential for recovery and recycling, which can provide both environmental and economic benefits.

Textile waste in landfill contributes to the formation of ‘leachate’ (the noxious fluid produced in landfill sites) as it decomposes, which has the potential to contaminate both surface and groundwater sources [6]. Another product of decomposition in landfill is methane gas, which is a major greenhouse gas and a significant contributor to global warming, although it can be used if collected. Textile waste is also incinerated in large quantities, and comes third after plastics and cardboard.

In the particular case of cotton based textiles, the process used to prepare the fabrics, generates byproducts in the form of cotton flocks. As can be seen in Figure 1, to produce cotton fabrics, on the first step, cotton fibers are yarned to manufacture high quality yarns. These yarns are the used to manufacture fabrics. The manufacturing process produces a large number of byproducts in the shape of fabric trims. These fabric trims are submitted to a defibration process, obtaining cotton fibers. These fibers are yarned and used for the manufacturing of fabrics that will be used to manufacture

denim. Anyhow, the defibration process produces fibers with length under 10mm. Such fibers are unable to be yarned and thus are a byproduct of the process without any value or use for the textile industry. This byproduct has the shape of cotton flocks. Moreover, as the yarns used are previously subjected to dying processes, these cotton flocks are composed by dyed fibers.

Although a lot of studies about the reinforcement of polypropylene with wood- and non-wood cellulose fibers can be found in the literature, only few of them report the use these cotton flocks byproduct as reinforcement for polypropylene-based composites [7-10]. The use of cotton waste is also limited as reinforcement of other polymers, with few publications in the literature [11].

One of the main limitations of the these composites is the maximum wt.% of cotton flocks content due to the flock aggregation without any prior treatment. In this sense, Petrucci et al. [9] use a pretreatment of the flocks with a vinyl-acetate water solution to obtain compressed sheets that are subsequently milled, then mixed with PP in a twin screen extruder and finally injection molded. The maximum amount of fiber introduced in this study was 16 wt.%. Araujo et al. [7] prepared composites with until 20 wt.% of reinforcement after dye removal and silanization or acetylation treatment. The composites in this case were mixed in a twin screen extruder and compression molded to form the composites.

In this work, waste dyed cotton flocks were used as reinforcement for polypropylene-based composites. The cotton flocks were used without any chemical treatment and only were cut down to ensure their correct individualization and dispersion in the matrix. Composites with 30 and 40 wt.% of waste cotton strands (WCS) were prepared. Percentages of polypropylene functionalized with maleic anhydre (MAPP) ranging from 0 to 8 wt.% were added to the composites to find the highest tensile strengths. The results showed tensile strengths higher than expected for the uncoupled composites. Then, the effect of the dye on the interphase was investigated by preparing composites reinforced with virgin cotton fibers. Additionally, the virgin cotton flocks were chemically analysed. A modified rule of mixtures was used to compute the intrinsic tensile strength of the WCS. Initially a good interphase was hypothesised for all the coupled composites. The intrinsic tensile strength of the dyed strands was found to be noticeably inferior to that of the virgin fibers, indicating a negative effect of the dye on the quality of the interphase. Single fiber tensile tests were carried out to obtain the tensile strength of the WCS. The obtained results were

submitted to a Weibull analysis to find the characteristic strength of the WCS. The results were tabulated against the fibers length and it was possible to find the characteristic strength of the WCS used in the composites, after its morphologic analysis. Then, the modified Kelly and Tyson equation was used to define the interfacial shear strength of the interphase and the orientation factor.

2 Materials and methods

2.1 Materials

The cotton flocks residues, treated with a reactive dye, from textile industry and with not enough length for spinning, were kindly supplied by Fontfilva S. L. (Olot, Girona, Spain). Figure 1 shows the aspect of the provided cotton residue flocks.

The polymer matrix used was polypropylene (PP) (Isplen PP090 62M) and was kindly supplied by Repsol-YPF (Tarragona, Spain). In order to improve the compatibility between cotton residues and PP, polypropylene functionalized with maleic anhydre (MAPP) (Epolene G3015), with an acid number of 15 mg KOH/g and Mn of 24800, was used as a coupling agent. This was acquired from Eastman Chemical Products (San Roque, Spain).

Sodium hydrosulphite ($Na_2S_2O_4$) was used to remove the dyes from the cotton residues and was provided by Sigma Aldrick (Barcelona, Spain). Decalin (Decahydronaphthalene) was acquired from Fischer Scientific (Madrid, Spain) and had 190ºC boiling point and 97% purity. This reagent was used to dissolve PP matrix in the fiber extraction from composites. All reactants used for cotton flocks characterization were bought from Scharlau Spain (Barcelona, Spain) and used without further purification.

2.2 Methods

2.2.1 Composite processing

The cotton residues were cut down to a nominal length of 1 mm using a blade mill in order to obtain a better dispersion in the composite. Then, PP, MAPP and cotton flocks residues were mixed at different wt./wt. ratios in an intensive melt mixer Brabender Plastograph (Brabender, Duisburg, Germany) at 185 ºC for 10 min, and at 80 rpm, in order to ensure to obtain a well-dispersed material. The blends were cut down to pellets with a particle size in the range of 10 mm using a pelletizer equipped with a set of knifes and different grids. The pellets were dried and stored at 80ºC for 24h. After

that, the composite blends were injection-moulded in a Meteor-40 injection machine (Mateu & Solé, Spain). The machine is equipped with three heating areas working at 175, 175 and 190 ºC, the highest temperature corresponding to the nozzle. First and second pressures were 120 and 37.5 $Kg.cm^{-2}$, respectively. This process allowed acquisition of specimens for mechanical characterization (ASTM D638).

2.2.2 Mechanical characterization

Processed materials were placed in a conditioning chamber (Dycometal) at 23ºC and 50% relative humidity during 48 hours, in accordance with ASTM D618, prior to testing. Afterwards, samples were mechanically studied by using a Universal testing machine (instrom TM 1122), fitted with a 5 kN load cell. Tensile specimens were shaped like a dog-bone (of approx. 160x13.3x3.2 mm), according to the ASTM D790 standard. Results were obtained from the average of at least 5 samples.

2.2.3 Fiber extraction from composites

Cotton residues were extracted from composites by matrix solubilisation using a Soxhlet apparatus and Decalin as a solvent. Small pieces of composites were cut and placed inside a specific cellulose filter and set into a Soxhlet equipment. A small cotton tab was used to prevent the fibers from getting out of the filtering tube. The fiber extraction was carried out during 24 hours. Afterwards, fibers were rinsed with acetone and then with distilled water in order to remove the solvent residue. Finally the fibers were dried in an oven at 105 ºC for 24 hours.

2.2.4 Determination of the fiber length and fiber diameter

Fiber length distribution and fiber diameter of the extracted cotton fibers were characterized by means of a Kajanni analyzer (FS-300). A diluted aqueous suspension (1 wt.% consistency) of fibers was analyzed during 2 to 5 minutes, and the length of the fibers was evaluated considering an amount of individual fibers in the range of 2500 to 3000 units. Minimums of two samples were analyzed. The Kajanni analyzer offers complete fiber, fines and shiv morphology characterization, but only the fiber length and fiber diameter distribution were used the present work.

The fibers were also measured with a Leica DMR-XA optic microscope with a 2µm optical resolution.

2.2.5 Cotton strands characterization

2.2.5.1 Degree of polymerisation

The degree of polymerisation (DP) of cotton fibers was determined according to UNE 57-039-92. The viscosimetric average molecular weight was calculated from the equation $\eta = K \cdot M^a$, where η is the intrinsic viscosity, K = 2.28 and a = 0.76 [12].

2.2.5.2 The solvent used was a copper (II) ethylenediamine by Scharlau Spain (Barcelona, Spain).Cationic demand

The cationic demand of cotton fiber was determined using a Mütek PCD 04 particle charge detector. First, 0.2 g (dried weight) of cotton fiber was diluted in 15 ml distilled water. Then 25 ml of cationic polymer polydiallyldimethylamonium chloride (polyDADMAC) was added to before fiber solution and it was mixed for 5 minutes with magnetic stirring. After this time the mixture was centrifuged in a Sigma Laborzentrifugen model 6 K 15 for 90 min at 4,000 rpm. Then, 10 ml of the supernatant was taken to the Mütek equipment. Anionic polymer (Pes-Na) was then added to the sample drop by drop with a pipette until the equipment reached 0 mV. The volume of anionic polymer consumed was used to calculate the cationic demand though:

$$CD = \frac{(C_{PD} \cdot V_{PD}) - (C_{AP} \cdot V_{AP})}{W_s} \quad (1)$$

where CD is the cationic demand (μeq/l), C_{PD} = cationic polymer concentration (g/l), V_{PD} = used volume of cationic polymer (ml), C_{AP} = anionic polymer concentration (g/l), V_{AP} = used volume of anionic polymer (ml) and W_S = sample's dry weight (g).

2.2.5.3 Chemical composition

Extractives and lignin of cotton fiber residues were determined following TAPPI standard methods, T222 om-88 and T223 cm-84, respectively. Cellulose content was measured according to Wise et al. (1946).

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2.2.5.4 Single fiber tensile test

The tensile strength of the cotton flocks was obtained from the force-displacement curves, following ASTM D3822-01 standard. The measurement was conducted using the INSTRON 5500R testing device (supplied by INSTRON, Cerdanyola del Vallès, Spain) equipped with 5kg force cell. The experiment was repeated at four different gauge lengths; 25.4, 19.05, 12.7 and 6.35 mm, using cross speed rates of 2.54, 1.905, 1.27 and 0.635 mm/min, respectively. An amount up to 100 single fibers was tested for each gauge length and the maximum force was evaluated.

The diameter of the fibers was determined by optical microscopy. Microscopy images were obtained and the width of the fibers was evaluated as a mean value of 3 measures

2.2.5.5 Fiber fading

To remove the dye from the cotton flocks, one dry gram of cotton residues was submerged into a hot Sodium hydrosulphite solution (25 wt.%) for two hours. Then, cotton flocks were water rinsed and dried at 50ºC.

3 Results and discussion

When hydrophilic natural fibers, as cotton, are used as reinforcement for a hydrophobic matrix, as PP, the use of coupling agents as MAPP is a common practice to obtain good tensile and flexural strength [13-15]. Consequently, searching the percentage of MAPP against fiber content that renders the best tensile strengths (σ_t^C) was the first step proposed by the authors to obtain competitive composite materials.

Figure 2 shows the behavior of the tensile strength of the PP-based composite materials containing 30 and 40 wt.% waste cotton strands (WCS) contents, when increasing contents of MAPP were added to the composite formulation.

It was found that adding MAPP increased progressively the tensile strength of the composites besides the reinforcement content. The composites with a 30 wt.% of WCS increased their tensile strength a 57.2, 63.7 and a 70.6% against the matrix when 2, 4 and 6% of MAPP was added, respectively. If the same values are compared with the composite without MAPP the respective increases were 13.6, 18.3 and 23.3%. Further MAPP contents caused a drop of the tensile strength of the composite. The most probable cause could be the self-entanglement of the MAPP chains [16]. The composites with a 40 wt.% content of WCS showed a similar behavior, with a maximum observed tensile strength when a 6% of MAPP was added to its formulation. Such MAPP content rendered 94.2 and 28.5% increases of the tensile strength, compared to the matrix and the uncoupled composite, respectively. While the increases against the matrix were found to be significant, the tensile strength of the uncoupled composites was found to be remarkably high [13, 17].

The uncoupled composite materials with 30 and 40 wt.% WCS increased the tensile strength of the matrix a 38.4 and a 51.1%, respectively. Such increases are really significant when compared with other uncoupled cellulosic fiber reinforced composites. A probable cause for such behavior could be due to the dye agents affecting surface

chemical character of the cotton flocks. In that sense, the cationic demand of the dyed cotton residue flocks, expressed in micro-equivalents of polyDACMAC per gram of reinforcement, was estimated at 16.39 µeq. g/g, while the virgin cotton fibers showed a 58.7 µeq. g/g demand [18]. The change on the superficial hydrophilicity of the dyed cotton is significant, increasing its hydrophobicity, and consequently increasing its affinity with the PP. The effect is similar to that obtained by diminishing the hydrophilic nature of natural fibers by surface treatment with alkyl ketene dimmer (AKD) [19, 20]. Then, some cotton residue flocks were faded, and their cationic demand was measured to be 48.9 µeq. g/g. Besides, some dyed and faded flocks were suspended in a water/hexane mixture (50/50%). Figure 3 shows the result.

It was found that the dyed and the faded cotton flocks had affinity with the organic phase (hexane), and aqueous phase, respectively. Consequently, it was apparent that the dying agents changed the surface character of the cotton fibers, increasing their hydrophobicity, and consequently their affinity with the PP, and thus resulting in comparatively high tensile strengths for the uncoupled composites [21].

Nonetheless, it is probable that such dying agents also affect the interactions of the cotton fiber surfaces with the MAPP, limiting its strengthening power. To that effect, a modified Rule of Mixtures (mRoM) was used to analyze the experimental results (Eq. 1).

$$\sigma_t^C = f_c \cdot \sigma_t^F \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \quad (1)$$

Were σ_t^C, σ_t^F *and* σ_t^{m*} are the tensile strength of the composite, the intrinsic tensile strength of the strands, and the tensile strength of the matrix at the composites' failure strain. The value of σ_t^{m*} was computed with a polynomial 4th regression of the stress strain curve of the matrix (Eq.2).

$$\sigma_t^{m*} = -0.0001 \cdot (\varepsilon_t^C)^5 + 0.0014 \cdot (\varepsilon_t^C)^4 + 0.0468 \cdot (\varepsilon_t^C)^3 - 1.1307 \cdot (\varepsilon_t^C)^2 + 9.0559 \cdot \varepsilon_t^C \quad (2)$$

V^F is the volume fraction of the reinforcement, and f_c is the coupling factor that is used to account for the effect of the fiber length and orientation, and the quality of the interface between the fibers and the matrix. It has been reported that bell bonded semi-aligned short fiber composites show coupling factor with 0.2 values [17, 22, 23].

The mRoM was used to obtain the value of the intrinsic tensile strengths of the cotton fibers, using the experimental results (Figure 3, Table 1), and a 0.2 coupling factor, assuming a high quality interphase in the case of the composites containing a 6% of MAPP.

The obtained σ_t^F were 658.2 and 624.5 MPa for the 30 and 40% coupled composites, respectively. Such intrinsic tensile strengths are sensibly higher to previously reported values [24, 25]. Nonetheless, if the dying agents affect the interactions between the fiber surface and the MAPP it means that the composites could not be defined as well bonded, and consequently, lower values of the coupling factor were expected. Anyhow, lower values of the coupling factor will produce higher intrinsic tensile strengths (a 0.15 coupling factor renders 1005 MPa intrinsic tensile strength). In the literature there are references to the intrinsic tensile strength of cotton fibers in the range from 287 to 800 MPa [26, 27]. The large variability of such value is common to natural fibers.

For comparison purposes, virgin cotton flocks were used to prepare a composite with a 20% of such fibers as reinforcement (the composite was coupled with a 6% of MAPP). Once tensile tested its tensile strength was 46.86 MPa and its strain at break was 4.9%. These new experimental data were used anew to back calculate the correspondent intrinsic tensile strength of virgin cotton flocks, by using the mRoM, and assuming a 0.2 coupling factor, obtaining a 1017.4 MPa value. The dyed and the virgin cotton strands are very similar, being its main difference the presence or not of dying agents and consequently its effect on the reactivity between the strands surface and the MAPP. Then, if the intrinsic strength of the cotton flocks is established at a value around 1000 MPa, it is clear that the coupling factor in the case of the dyed cotton strands-based composites is lower than 0.2, and such composites could not considered fully well bonded. It is known that the contribution of a reinforcing fiber to the tensile strength of a composite depends on its intrinsic tensile strength, but also in the nature of the bonds between the matrix and the fibers, and the number of such bonds per volume fraction. These virgin cotton flocks were chemically analyzed (table 2), and their chemical composition and its degree of polymerization (DP) further support high intrinsic tensile strengths for such fibers.

It was found that the cellulose and the alpha-cellulose contents, and its degree of polymerization were comparatively very high. A bleached pine Kraft pulp (BPKP) shows lesser cellulose contents (84.1 wt.%, with a 15.9 wt.% of hemicelluloses), and a polymerization degree of 1197. A PP-based composite material reinforced with a 40 wt.% of BPKP, coupled with a 6% of MAPP reported that the intrinsic tensile strength of the BPKP is 474.6 MPa. The qualitative and quantitative differences with the cotton

fibers are clear. With the objective of clarifying the value of the intrinsic tensile strength of the cotton flocks single fiber tensile tests were performed.

3.1 Cotton flocks intrinsic mechanical properties.

Figure 4 shows two representative samples of the evaluation of the mean diameter (width) of the fibers submitted to single fiber tensile test.

The width of the single fibers was very regular, fiber to fiber, with slight variation between them. The mean diameter of all the evaluated fibers was 17.35 µm. Then, the fibers were submitted to tensile test. Figure 5 shows the results of the single fiber tests against the gauge length.

The intrinsic properties of the Cotton fibers were computed after a Weibull analysis of the single fiber tests experimental results. The Weibull analysis describes the probability of failure of a fiber under stress. The probability of failure under a given stress (σ) is directly linked to the presence of a defect in the fiber surface with the size that allows crack propagation [28]. The failure stress is distributed accordingly to a Weibull distribution, described by equation 3:

$$P_f(\sigma) = 1 - e^{\left[-\left(\frac{\sigma}{\eta}\right)^{\beta}\right]} \quad (3)$$

Where, β is known as the Weibull modulus, and is a measure of the dispersion of the strength values. The higher the Weibull modulus is, the shorter is the scatter of the strength values. In the same equation, σ and η are the measured fiber tensile strengths, and the scale factor or the characteristic strength of the fiber. With the objective of measuring the intrinsic tensile strength of the fibers the gauge length of the Instron universal dynamometer were established at four different positions; 1, ¾, ½, and ¼ inches (25.40, 19.05, 12.70 and 6.35mm). At least 100 fibers were tested for each gauge lengths. The strength of a fiber is highly dependent on its length, as the higher the length, higher id the probability of finding a defect. Besides, natural fibers usually show high standard deviations on their mechanical properties, thus a scatter on their properties was expected. Upper and lower strength values were omitted in agreement with the research by Thomason [29].

Figure 6 shows the linearized representation of the probability of failure against the natural logarithm of the measured intrinsic fiber tensile strength.

Table 2 shows the experimental mean intrinsic tensile strengths (σ_t^F) and its standard deviations. As expected the experimental values were higher for the shorter fibers. For comparison purposes the table also adds the specific mean tensile strengths of the fibers ($\sigma_{t\ ,\ specific}^F$). In that sense, the specific intrinsic tensile strength of a glass fiber is around 580 MPa/g cm^3, and a flax fiber around 600 MPa/g cm^3 [30]. The Weibull modulus and the characteristic strengths were computed after the statistical analysis and are also shown in table 3.

The low value of the Weibull modulus reflects the exhibited wide scatter. The measured mean intrinsic tensile strengths are similar to their respective characteristic strengths. The characteristic strengths also visualize the highest probability of failure for the longest fibers. Figure 5 shows a linear evolution of the tensile strength of the single fibers against the gauge length. This gauge length is equivalent to the fiber length and a linear regression of the intrinsic tensile strength of the fibers (σ_t^F) against its length (L^F) delivers Eq. 3:

$$\sigma_t^F = 952 - 16.504 \cdot L^F \quad (3)$$

Usually the mean lengths of the fibers inside the composites show values much shorter than that of the gauge lengths. The regression equation can be used to compute the intrinsic tensile strength of the reinforcing fibers, once such fibers are morphologically characterized. This morphological analysis indicated that the mean diameter of the fibers was 16.5 µm. Figure 7 shows the length distribution of the cotton fibers extracted from the matrix, for the case of the coupled composite with a 40% of WCS.

It was found that the mean arithmetic lengths of the coupled composites with 30 and 40 wt.% WCS contents were 239 and 210 µm, respectively. In the same way, the respective single weighted length was 374 and 339 µm. The equation presented with the figure 5 was used to compute the respective intrinsic tensile strength; obtaining 948.0 and 948.5 MPa values for the 239 and 210 µm mean lengths, respectively. The values are very similar to those obtained by using the mRoM while assuming a good interphase. Nonetheless, there are studies that observe notable differences between the intrinsic tensile strengths of the fibers if a re experimentally measured or back-computed by using micromechanical models [31].

With the morphologic data of the reinforcing fibers and the results of the tensile tests of the matrix and the composites it was possible to use the modified Kelly and Tyson model [32-34] (Eq. 4) to assess the quality of the interphase.

$$\sigma_t^C = \chi_1\left(\sum_i\left[\frac{\tau\cdot l_i^F\cdot V_i^F}{d^F}\right]+\sum_j\left[\sigma_t^F\cdot V_j^F\left(1-\frac{\sigma_t^F\cdot d^F}{4\cdot\tau\cdot l_j^F}\right)\right]\right)+(1-V^F)\cdot\sigma_t^{m*} \qquad (4)$$

In Equation 4 the d^F and $l^F_{i,j}$ terms represent the fiber diameter and length, respectively. χ_1 is the orientation factor, modifying the original Kelly and Tyson model, developed for aligned reinforcements. Finally, τ is the interfacial shear strength, accounting for the ability of the interphase to transmit loads from the matrix to the fiber [35].

Previous works found that the orientation angle was highly influenced by the machinery used during the mould injection of the specimens. It was found that such parameter also rendered values between 0.25 and 0.35. It is accepted that the relation between the orientation factor and the mean orientation angle (α) is represented by: $\alpha=cos^4(\chi_1)$. Accordingly, the mean orientation angles were between 40 and 45º. It is also known that Von Mises criteria: $\tau=\sigma_t^c/3^{1/2}$ could be used to predict the value of the interfacial shear strength in the case of very good interphases, and also an upper bound for such value (cites). As the used PP had an tensile strength of 27.6 MPa, Von Mises criteria establishes a 15.9 MPa value for τ.

A numerical solution for the Kelly and Tyson equation was proposed in order to know the value of the interfacial shear strength and the orientation factor for the composites that added a 6% of MAPP. If the equation is handled individually for both composites shows two incognita, being impossible to solve. On the other hand it is wise thinking that both values will be similar for the composites with a 40 and 30% of cotton fiber reinforcement, being the case in previous researches [17, 23]. Thus, a numerical iterative method was applied to find a value for the interfacial shear strength and the orientation factor for both composites that showed the lowest distance between the computed values. The initialization values were a 0.3 orientation factor and 16 MPa interfacial shear strength. The method converged very fast to interfacial shear strengths around 14.8 MPa and an orientation factors in the range from 0.33 to 0.34. The interfacial shear strength was inferior to Von Mises, showing that the interphase has possibilities to be improved, supporting that the dye somehow limited the interaction between the fibers and the polymer. At the same time, the orientation factor was inside the 0.25 to 0.35 range found in previous works [14, 17]. Besides the value coincides with the mean value of the orientation factor predicted by other researchers [36]. The

orientation factor was used to compute the theoretical interfacial shear strength of the uncoupled composites, obtaining 6.5 and 8.3 MPa values for the 30 and 40% composites, respectively. Such values are in line with those shown by other natural fiber reinforced polypropylene composites [17, 23].

Finally, the mRoM (Eq.1) was used to compute the value of the coupling factor of the coupled and uncoupled WCS-based composites. The coupled composites with 30 and 40 wt.% WCS contents rendered 0.159 and 0.146 coupling factor values, respectively. The value is far from 0.2, pointing out improvable interphases, and further adding to the negative effect of the dyes on such interphases. On the other hand, the same uncoupled composites showed coupling 0.117 and 0.105 coupling factors, respectively. Such values are high in comparison with other natural fiber uncoupled composites, which show slightly positive values [13, 23, 37, 38].

4 Conclusions

A by-product of the textile industry in the shape of waste cotton flocks was used to reinforce polypropylene. This use could inertize such by-product and extend the value chain of the textile industries.

It was found that the organic dyes favored the interphase between the cotton flocks and the matrix, as long as their composite materials showed comparatively relevant tensile strength, without any coupling agent. At the same time, it was apparent that the aforementioned dyes affected negatively the action of the coupling agents.

The tested cotton flocks presented intrinsic tensile strengths superior to that found in the bibliography. With such strengths, its composites could replace glass fiber-based reinforced composites.

The intrinsic tensile strengths of the cotton flocks were obtained by single fiber tensile test, and as it is known that the fibers suffer morphologic changes when composed. Thus, it is probable that its intrinsic tensile strength inside the composite is different to that outside. A more accurate micro-mechanics analysis could unveil possible deviations from the experimental values.

The interfacial tensile strength and the orientation factor obtained in the analysis are consistent with the literature.

436 **References**
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438 [1] Mishra R, Behera B, Militky J. Recycling of Textile Waste Into Green Composites:
439 Performance Characterization. Polymer Composites. 2014;35(10):1960-7.
440 [2] DeVallance DB, Gray J, Lentz H. PROPERTIES OF WOOD/RECYCLED TEXTILE
441 COMPOSITE PANELS. Wood Fiber Sci. 2012;44(3):310-8.
442 [3] Mulinari DR, Voorwald HJC, Cioffi MOH, Lima CAA, Baptista C, Rocha GJM.
443 Composite materials obtained from textile fiber residue. Journal of Composite
444 Materials. 2011;45(5):543-7.
445 [4] Barbero-Barrera MdM, Pombo O, Navacerrada MdlÁ. Textile fibre waste
446 bindered with natural hydraulic lime. Composites Part B: Engineering. 2016;94:26-
447 33.
448 [5] Ryu C, Phan AN, Sharifi VN, Swithenbank J. Combustion of textile residues in a
449 packed bed. Exp Therm Fluid Sci. 2007;31(8):887-95.
450 [6] Jha MK, Kumar V, Maharaj L, Singh RJ. Studies on leaching and recycling of zinc
451 from rayon waste sludge. Industrial & Engineering Chemistry Research.
452 2004;43(5):1284-95.
453 [7] Araújo RS, Rezende CC, Marques MF, Ferreira LC, Russo P, Emanuela Errico M,
454 et al. Polypropylene‐based composites reinforced with textile wastes. J Appl
455 Polym Sci. 2017.
456 [8] Haque MS. Processing and characterization of waste denim fiber reinforced
457 polymer composites. 2014.
458 [9] Petrucci R, Nisini E, Puglia D, Sarasini F, Rallini M, Santulli C, et al. Tensile and
459 fatigue characterisation of textile cotton waste/polypropylene laminates.
460 Composites Part B: Engineering. 2015;81:84-90.
461 [10] Taşdemır M, Koçak D, Usta I, Akalin M, Merdan N. Properties of polypropylene
462 composite produced with silk and cotton fiber waste as reinforcement.
463 International Journal of Polymeric Materials. 2007;56(12):1155-65.
464 [11] Tserki V, Matzinos P, Panayiotou C. Effect of compatibilization on the
465 performance of biodegradable composites using cotton fiber waste as filler. J Appl
466 Polym Sci. 2003;88(7):1825-35.
467 [12] Henriksson M, Berglund LA, Isaksson P, Lindstrom T, Nishino T. Cellulose
468 nanopaper structures of high toughness. Biomacromolecules. 2008;9(6):1579-85.
469 [13] Reixach R, Espinach FX, Arbat G, Julián F, Delgado-Aguilar M, Puig J, et al.
470 Tensile Properties of Polypropylene Composites Reinforced with Mechanical,
471 Thermomechanical, and Chemi-Thermomechanical Pulps from Orange Pruning.
472 BioResources. 2015;10(3):4544-56.
473 [14] Granda LA, Espinach FX, Lopez F, Garcia JC, Delgado-Aguilar M, Mutje P.
474 Semichemical fibres of Leucaena collinsii reinforced polypropylene:
475 Macromechanical and micromechanical analysis. Compos Pt B-Eng. 2016;91:384-
476 91.
477 [15] Li Y, Pickering KL, Farrell RL. Determination of interfacial shear strength of
478 white rot fungi treated hemp fibre reinforced polypropylene. Composites Science
479 and Technology. 2009;69(7-8):1165-71.
480 [16] Beckermann GW, Pickering KL. Engineering and evaluation of hemp fibre
481 reinforced polypropylene composites: Micro-mechanics and strength prediction
482 modelling. Composites Part A-Applied Science and Manufacturing.
483 2009;40(2):210-7.

[17] Vallejos ME, Espinach FX, Julian F, Torres L, Vilaseca F, Mutje P. Micromechanics of hemp strands in polypropylene composites. Composites Science and Technology. 2012;72(10):1209-13.
[18] Carrasco F, Mutjé P, Pelach MA. Control of retention in paper-making by colloid titration and zeta potential techniques. Wood Science and Technology. 1998;32(2):145-55.
[19] Mutje P, Girones J, Lopez A, Llop MF, Vilaseca F. Hemp strands: PP composites by injection molding: Effect of low cost physico-chemical treatments. Journal of Reinforced Plastics and Composites. 2006;25(3):313-27.
[20] Vilaseca F, Lopez A, Llauro X, Pelach MA, Mutje P. Hemp strands as reinforcement of polystyrene composites. Chemical Engineering Research & Design. 2004;82(A11):1425-31.
[21] Zhou Y, Fan M, Chen L. Interface and bonding mechanisms of plant fibre composites: An overview. Composites Part B: Engineering. 2016;101:31-45.
[22] Sanadi AR, Young RA, Clemons C, Rowell RM. Recycled newspaper fibers as reinforcing fillers in thermoplastic: 1 analysis of tensile and impact properties in polypropylene Journal of Reinforced Plastics and Composites. 1994;13(1):54-67.
[23] Reixach R, Franco-Marquès E, El Mansouri N-E, de Cartagena FR, Arbat G, Espinach FX, et al. Micromechanics of Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulp from Orange Tree Pruning as Polypropylene Reinforcement: A Comparative Study. BioResources. 2013;8(3).
[24] Kompella MK, Lambros J. Micromechanical characterization of cellulose fibers. Polymer Testing. 2002;21(5):523-30.
[25] Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. Progress in Polymer Science. 1999;24(2):221-74.
[26] Yan L, Kasal B, Huang L. A review of recent research on the use of cellulosic fibres, their fibre fabric reinforced cementitious, geo-polymer and polymer composites in civil engineering. Composites Part B: Engineering. 2016;92:94-132.
[27] Kong C, Lee H, Park H. Design and manufacturing of automobile hood using natural composite structure. Composites Part B: Engineering. 2016;91:18-26.
[28] Rösler J, Harders H, Baeker M. Mechanical behaviour of engineering materials: metals, ceramics, polymers, and composites: Springer Science & Business Media; 2007.
[29] Thomason J. On the application of Weibull analysis to experimentally determined single fibre strength distributions. Composites Science and Technology. 2013;77:74-80.
[30] Cañigueral N, Vilaseca F, Méndez JA, López JP, Barberà L, Puig J, et al. Behavior of biocomposite materials from flax strands and starch-based biopolymer. Chemical Engineering Science. 2009;64(11):2651-8.
[31] Shah DU, Nag RK, Clifford MJ. Why do we observe significant differences between measured and 'back-calculated' properties of natural fibres? Cellulose. 2016;23(3):1481-90.
[32] Kelly A, Tyson W. Tensile porperties of fibre-reinforced metals - copper/tungsten and copper/molybdenum. Journal of the Mechanics and Physics of Solids. 1965;13(6):329-38.
[33] Espinach FX, Granda LA, Tarrés Q, Duran J, Fullana-i-Palmer P, Mutjé P. Mechanical and micromechanical tensile strength of eucalyptus bleached fibers reinforced polyoxymethylene composites. Composites Part B: Engineering. 2017;116:333-9.

[34] Granda LA, Espinach FX, López F, García JC, Delgado-Aguilar M, Mutjé P. Semichemical fibres of Leucaena collinsii reinforced polypropylene: Macromechanical and micromechanical analysis. Composites Part B: Engineering. 2016;91:384-91.
[35] Serrano A, Espinach FX, Julian F, del Rey R, Mendez JA, Mutje P. Estimation of the interfacial shears strength, orientation factor and mean equivalent intrinsic tensile strength in old newspaper fiber / polypropylene composites. Composites Part B: Engineering. 2013(50):232-8.
[36] Fu SY, Lauke B. Effects of fiber length and fiber orientation distributions on the tensile strength of short-fiber-reinforced polymers. Composites Science and Technology. 1996;56(10):1179-90.
[37] Serrano A, Espinach FX, Tresserras J, del Rey R, Pellicer N, Mutje P. Macro and micromechanics analysis of short fiber composites stiffness: The case of old newspaper fibers-polypropylene composites. Materials & Design. 2014;55:319-24.
[38] Lopez JP, Mendez JA, Espinach FX, Julian F, Mutje P, Vilaseca F. Tensile Strength characteristics of Polypropylene composites reinforced with Stone Groundwood fibers from Softwood. BioResources. 2012;7(3):3188-200.

Figure Captions

Figure 1: Cotton textiles manufacturing roadmap.

Figure 2: Tensile strength of the composites against its MAPP content. (a) Composites with a 30% of cotton strands, (b) composites with a 40% of cotton strands

Figure 3: Dyed and faded cotton residue suspended in a water/hexane mixture.

Figure 4: Evaluation of the mean diameter of the single cotton fibers.

Figure 5: Intrinsic tensile strength of the dyed cotton strands submitted to single fiber tensile test, against the gauge length

Figure 62: Linearized cumulative probability of failure against the natural logarithm of the measured fiber tensile strengths for each gauge length.

Figure 7: Fiber length distribution of the WCS extracted from the 40% reinforced coupled composite.

Tables

Table 1: Experimental results used to solve the mRoM

Fiber type	Fiber Content (%)	MAPP (%)	V^F	ε_t^C *(%)*	σ_t^{m*} *(Mpa)*
WCS	30	0	0.205	3.5	20.0
WCS	40	0	0.287	3.3	19.4
WCS	30	6	0.205	3.9	21.1
WCS	40	6	0.287	3.7	20.6
Virgin cotton	20	6	0.131	4.9	23.2

565

566 **Table 2: Chemical composition of the Surface and degree of polymerization of the virgin cotton strands**

Cellulose	α cellulose	Lignin	Extractives	Ash	Others	D. P.
93.8%	89.95%	0.55%	2.85%	1.15%	1.15%	4727

567

568 **Table 3: Experimental mean intrinsic tensile strengths of the fibers, and the Weibull analysis**

569 **outputs.**

Gauge length (mm)	σ_t^F ± SD (MPa)	$\sigma^F_{t,\text{ specific}}$ (MPa/g cm^3)	Weibull shape factor β	Characteristic strength η (MPa)
6.35	739 ± 356	493	2.2	854
12.70	638 ± 310	425	2.3	735
19.05	540 ± 273	360	2.4	632
25.40	478 ± 256	319	2.4	539

570

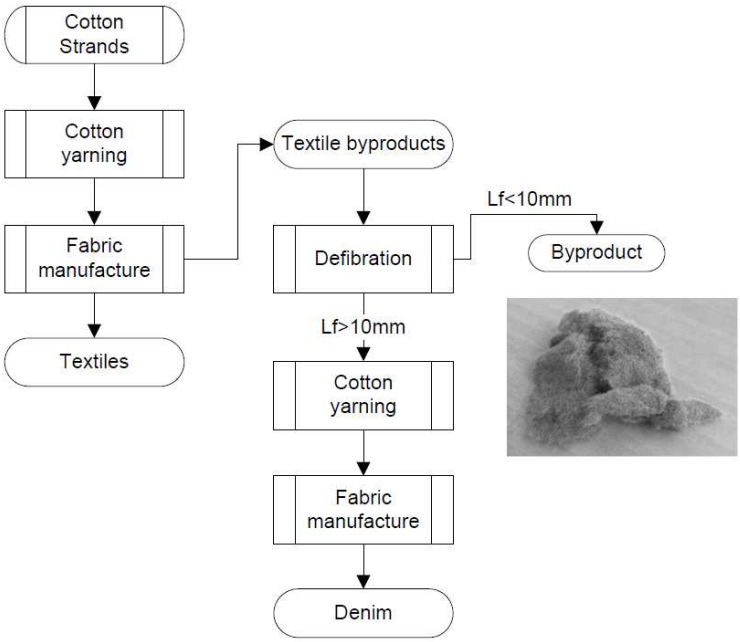

Figure 1: Cotton textiles manufacturing roadmap.

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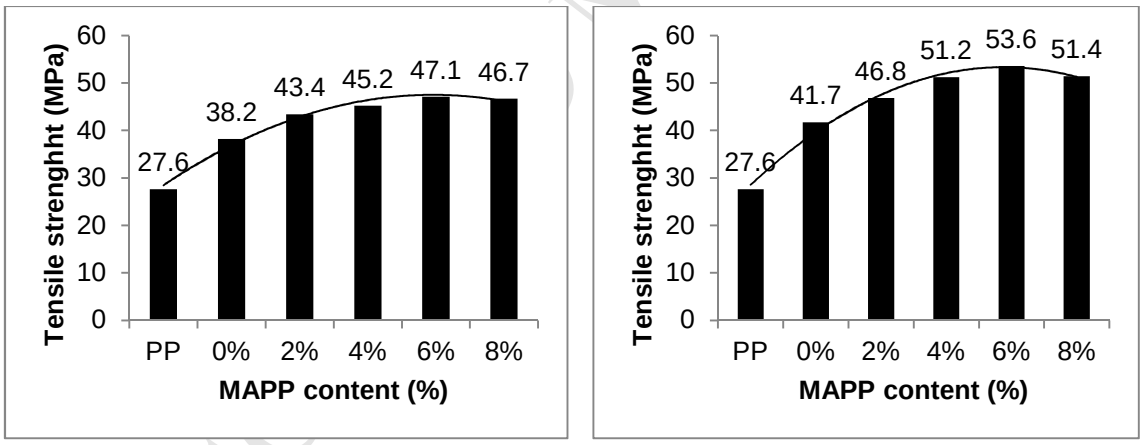

a b

Figure 2: Tensile strength of the composites against its MAPP content. (a) composites with a 30% of cotton strands, (b) composites with a 40% of cotton strands

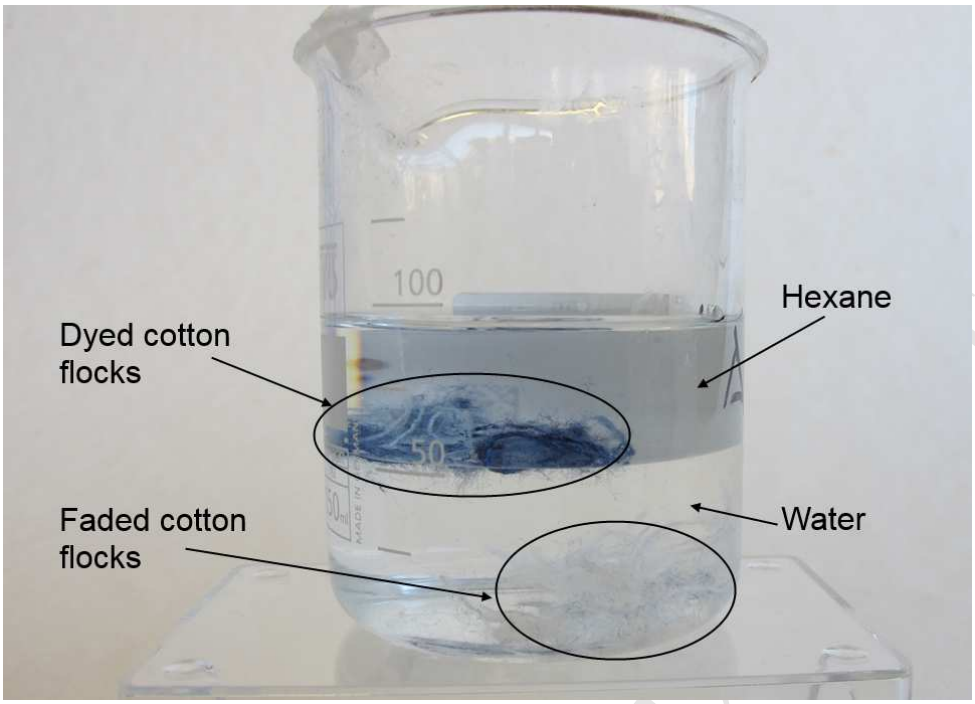

Figure 3: Dyed and faded cotton residue suspended in a water/hexane mixture.

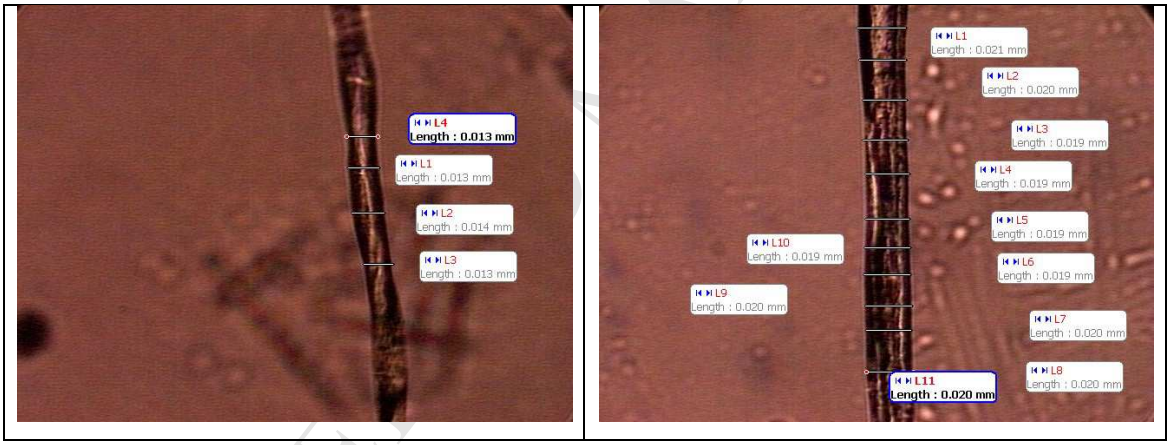

Figure 4: Evaluation of the mean diameter of the single cotton fibers.

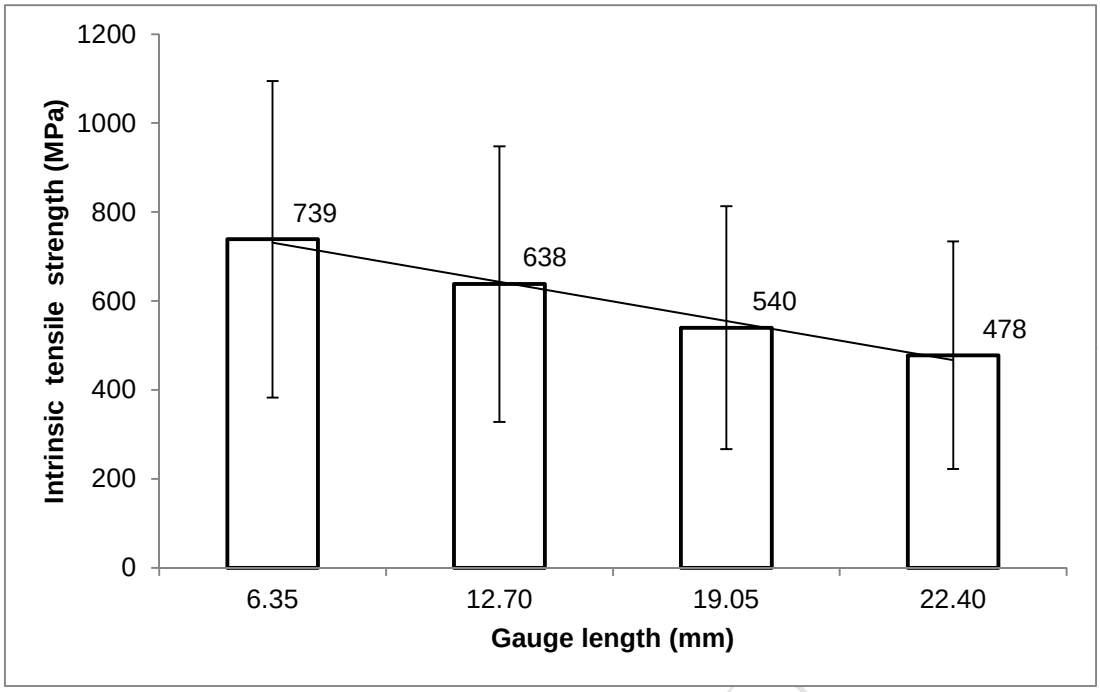

Figure 5: Intrinsic tensile strength of the dyed cotton strands submitted to single fiber tensile test, against the gauge length

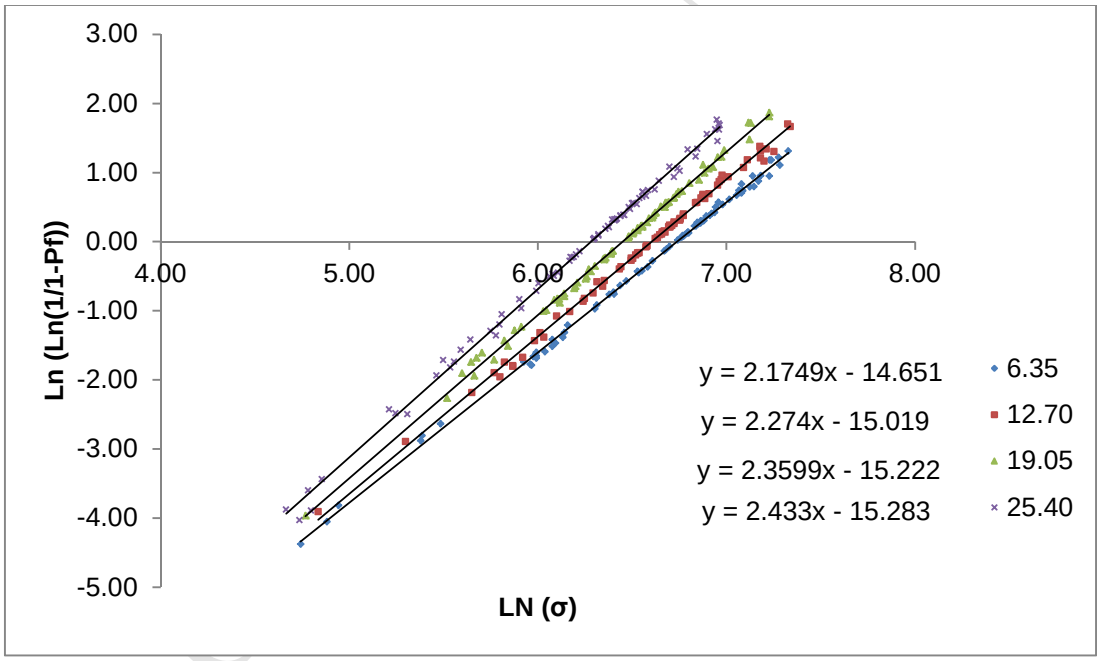

Figure 6: Linearized cumulative probability of failure against the natural logarithm of the measured fiber tensile strengths for each gauge length.

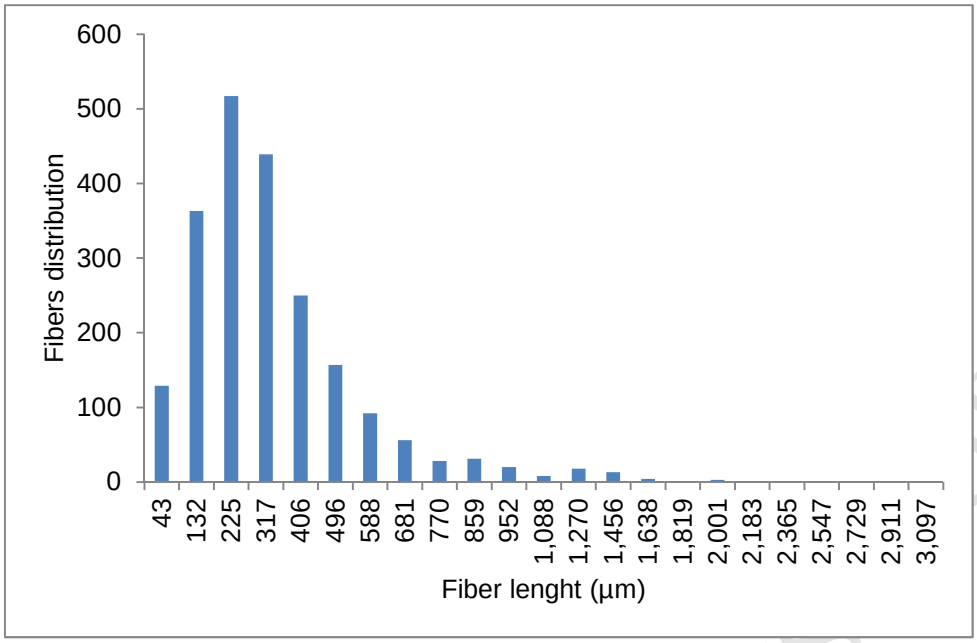

Figure 7: Fiber length distribution of the WCS extracted from the 40% reinforced coupled composite.